Application For Letters Patent
Of The United States

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Title of Invention:

CELLULOSE ESTER FILM, ITS MANUFACTURING
METHOD, POLARIZING PLATE, AND LIQUID
CRYSTAL DISPLAY

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To All Whom It May Concern:
The following is a specification
of the aforesaid Invention:

CELLULOSE ESTER FILM, ITS MANUFACTURING METHOD,

POLARIZING PLATE, AND LIQUID CRYSTAL DISPLAY

FIELD OF THE INVENTION

The present invention relates to a cellulose ester film
and its manufacturing method, and particularly to a cellulose
ester film useful for a protective film of polarizing plate,
and a polarizing plate and a liquid crystal display each
employing the cellulose ester film.

BACKGROUND OF THE INVENTION

Recently, development has been made regarding decrease
in thickness and weight of a note board type personal
computer. In parallel with this development, a polarizing
plate used in a device such a liquid crystal display or an
organic EL display has been eagerly sought to be increasingly
thinner. Particularly, decrease in thickness of a protective

film of a polarizing plate has been strongly required.

However, it has been proved that a simple decrease in

thickness of the polarizing plate protective film produces

various problems. One of the problems regards moisture vapor

permeation (moisture vapor transmittance). For example, as

the thickness of a polarizing plate protective film

decreases, the moisture vapor transmittance of the film

becomes higher, resulting in lowering of durability of the

polarizing plate. There have been proposed several methods

in which moisture vapor transmittance is optimized. A film

with a lower moisture vapor transmittance improves durability

of a polarizing plate employing the film, however, too low

moisture vapor transmittance has a defect in that an adhesive

is difficult to be dried which is used to adhere a polarizing

plate protective film to a polarizing film.

Therefore, a polarizing plate protective film with

moisture vapor permeation property satisfying both the

durability and the drying property is required. A cellulose

ester film is used in most of polarizing plate protective

films, and moisture vapor transmittance of the polarizing

plate protective film employing the cellulose ester film is

markedly deteriorated due to decrease in thickness. It is

known that the high content of a plasticizer in the

polarizing plate protective film improves a moisture vapor
transmittance, however, a too high content of the plasticizer
in the film causes problem of lowering dimensional stability
of the film. A polarizing plate protective film having an
excellent moisture vapor permeation property and an excellent
film performance is required.

SUMMARY OF THE INVENTION

The present invention has been made in view of the
above. An object of the invention is to provide a cellulose
ester film having an excellent moisture vapor transmittance
and excellent dimensional stability and a manufacturing
method thereof. Another object of the invention is to
provide a cellulose ester film having excellent resistance to
high temperature and high humidity and excellent UV light
fastness, which is suitable for a polarizing plate protective
film and a polarizing plate and a liquid crystal display each
employing the film.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1(a) is a schematic view showing a first
embodiment of a solution cast film manufacture process.

Fig. 1(b) is a schematic view showing a second embodiment of a solution cast film manufacture process.

Fig. 1(c) is a schematic view showing a third embodiment of a solution cast film manufacture process.
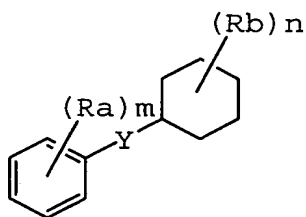
Fig. 1(d) is a schematic view showing a fourth embodiment of a solution cast film manufacture process.

DETAILED DESCRIPTION OF THE INVENTION

The present invention can be attained by the following constitutions:

1. A cellulose ester film comprising a compound represented by the following formula (1) in an amount of 1 to 30% by weight

formula (1)

wherein Y represents an ester bond or a divalent organic group containing an ester bond, Ra and Rb independently represent a substituent, and m and n independently represent an integer of from 0 to 5, provided that when m or n is not less than 2, plural Ras or Rbs may be the same or different.

2. The cellulose ester film of item 1, wherein the divalent organic group containing an ester bond represented by Y represents $-R^1C(=O)O-$; $-C(=O)OR^2-$; $-C(=O)O-R^3-OC(=O)-$; or $-OC(=O)-R^4-C(=O)O-$, in which R^1 and R^2 independently represent a substituted or unsubstituted alkylene group, and R^3 and R^4 independently represent a substituted or unsubstituted alkylene group, or $-(R^5O)_pR^5-$, in which R^5 represents a substituted or unsubstituted alkylene group, and p is an integer of from 1 to 3; the substituent represented by Ra or Rb is an alkyl group, $RcC(=O)O-$ or $-C(=O)ORc$ in which Rc represents a substituted or unsubstituted phenyl group or a substituted or unsubstituted cyclohexyl group, and m and n independently represent an integer of from 0 to 5, provided that when m or n is not less than 2, plural Ras or Rbs may be the same or different.

3. The cellulose ester film of item 2, wherein the unsubstituted alkylene group represented by R^1, R^2, R^3, R^4 or R^5 represents methylene, ethylene, trimethylene, propylene, tetramethylene, butylene, pentamethylene, or pentylene, and the substituted alkylene group represented by R^1, R^2, R^3, R^4 or R^5 represents methylene, ethylene, trimethylene, propylene, tetramethylene, butylene, pentamethylene, or pentylene, each having methyl, ethyl, n- or iso-propyl, n-,

iso-, or tert-butyl, acetoxy, phenylcarbonyloxy, cyclohexylcarbonyloxy, phenylcarbonyloxymethyl or cyclohexylcarbonyloxymethyl as a substituent.

4. The cellulose ester film of item 2, wherein the substituent represented by Ra or Rb is RcC(=O)O- or -C(=O)ORc in which Rc represents a substituted or unsubstituted phenyl group or a substituted or unsubstituted cyclohexyl group, and m represents an integer of from 1 to 5.

5. The cellulose ester film of item 2, wherein the substituent represented by Ra or Rb is RcC(=O)O- or -C(=O)ORc in which Rc represents a substituted or unsubstituted phenyl group or a substituted or unsubstituted cyclohexyl group, and n represents an integer of from 1 to 5.

6. The cellulose ester film of item 2, wherein Ra is RcC(=O)O- or -C(=O)ORc in which Rc represents a substituted or unsubstituted cyclohexyl group, and m represents an integer of from 1 to 5.

7. The cellulose ester film of item 1, wherein the cellulose ester film comprises a UV absorbent having a distribution coefficient of not less than 8.5.

8. The cellulose ester film of item 1, wherein the cellulose ester film comprises silicon oxide particles.

9. The cellulose ester film of item 1, wherein the cellulose ester film comprises a cellulose ester having a total acyl substitution degree of from 2.55 to 2.85.

10. The cellulose ester film of item 1, wherein the cellulose ester film has a thickness of from 10 to 60 μm, a moisture vapor transmittance of from 20 to 200 $g/m^2 \cdot 24$ hr, and a rate of weight change falling within the range of ± 2% in which the rate is represented by the ratio of the difference between the film weights before and after storage at 80° C and 90% RH for 48 hours to the film weight before the storage.

11. A method of manufacturing a cellulose ester film according to a solution cast film manufacturing process, the method comprising the steps of casting on a support a cellulose ester solution comprising a compound represented by formula (1) of item 1 above to form a web on the support, drying the web for 30 to 90 seconds on the support, peeling the web from the support, and further drying the peeled web.

12. The method of item 11, wherein the cellulose ester film comprises the compound in an amount of from 1 to 30% by weight.

13. The method of item 11, wherein in formula (1), the divalent organic group containing an ester bond represented by Y represents $-R^1C(=O)O-$; $-C(=O)OR^2-$; $-C(=O)O-R^3-OC(=O)-$; or $-OC(=O)-R^4-C(=O)O-$, in which R^1 and R^2 independently represent a substituted or unsubstituted alkylene group, and R^3 and R^4 independently represent a substituted or unsubstituted alkylene group, or $-(R^5O)_pR^5-$, in which R^5 represents a substituted or unsubstituted alkylene group, and p is an integer of from 1 to 3; the substituent represented by Ra or Rb is an alkyl group, RcC(=O)O- or -C(=O)ORc in which Rc represents a substituted or unsubstituted phenyl group or a substituted or unsubstituted cyclohexyl group, and m and n independently represent an integer of from 0 to 5, provided that when m or n is not less than 2, plural Ras or Rbs may be the same or different.

14. The method of item11, wherein the cellulose ester film comprises a UV absorbent having a distribution coefficient of not less than 8.5.

15. The method of item 11, wherein the cellulose ester film comprises silicon oxide particles.

16. The method of item 11, wherein the cellulose ester film comprises a cellulose ester having a total acyl substitution degree of from 2.55 to 2.85.
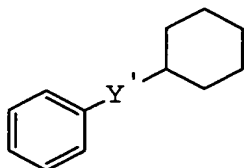
17. The method of item 11, wherein the cellulose ester film has a thickness of from 10 to 60 μm, a moisture vapor transmittance of from 20 to 200 $g/m^2 \cdot 24$ hr, and a rate of weight change falling within the range of ±2% in which the rate is represented by the ratio of the difference between the film weights before and after storage at 80° C and 90% RH for 48 hours to the film weight before the storage.

18. The method of item 11, wherein the cellulose ester solution contains methyl acetate.

19. A polarizing plate comprising the cellulose ester film of item 1.

20. A liquid crystal display employing the polarizing plate of item 19.

41. A cellulose ester film comprising a compound having a structure represented by the following formula (1') in an amount of from 1 to 30% by weight,

formula (1')

wherein Y′ represents a divalent organic group, and at least one of the aromatic ring and the cyclohexane ring may have a substituent.

42. The cellulose ester film of item 41 above, wherein Y′ in formula (1′) is a divalent organic group containing an ester bond.

43. The cellulose ester film of item 41 or 42 above, wherein the cellulose ester film comprises a UV absorbent having a distribution coefficient of not less than 8.5.

44. The cellulose ester film of any one of items 41 through 43 above, wherein the cellulose ester film comprises silicon oxide particles.

45. The cellulose ester film of any one of items 41 through 44 above, wherein the cellulose ester film comprises a cellulose ester having a total substitution degree of from 2.55 to 2.85.

46. The cellulose ester film of any one of items 41 through 45 above, wherein the cellulose ester film has a thickness of from 10 to 60 μm, a moisture vapor transmittance of from 20 to 200 $g/m^2 \cdot 24$ hr, and a rate of weight change falling within the range of ±2% in which the rate is represented by the ratio of the difference between the film

weights before and after storage at 80° C and 90% RH for 48 hours to the film weight before the storage.

47. A method of manufacturing a cellulose ester film according to a solution cast film manufacturing process, the method comprising the steps of casting on a support a cellulose ester solution comprising a compound having a structure represented by formula (1') above to form a web on the support, drying the web for 30 to 90 seconds on the support, peeling the web from the support, and further drying the peeled web.

48. The method of item 47 above, wherein the cellulose ester film comprises the compound in an amount of from 1 to 30% by weight.

49. The method of items 47 or 48 above, wherein Y' in formula (1') is a divalent organic group containing an ester bond.

50. The method of any one of items 47 through 49 above, wherein the cellulose ester film comprises a UV absorbent having a distribution coefficient of not less than 8.5.

51. The method of any one of items 47 through 50 above, wherein the cellulose ester film comprises silicon oxide particles.

52. The method of any one of items 47 through 51 above, wherein the cellulose ester film comprises a cellulose ester having a total substitution degree of from 2.55 to 2.85.

53. The method of any one of items 47 through 52 above, wherein the cellulose ester film has a thickness of from 10 to 60 μm, a moisture vapor transmittance of from 20 to 200 $g/m^2 \cdot 24$ hr, and a rate of weight change falling within the range of $\pm 2\%$ in which the rate is represented by the ratio of the difference between the film weights before and after storage at 80° C and 90% RH for 48 hours to the film weight before the storage.

54. The method of any one of items 47 through 53 above, wherein the cellulose ester solution contains methyl acetate.

55. A polarizing plate comprising the cellulose ester film of any one of items 41 through 46 above.

56. A liquid crystal display employing the polarizing plate of item 55 above.

The present inventors have made an extensive study in order to solve the problems described previously, and as a result, they have succeeded in obtaining a cellulose ester film which provides a satisfactory moisture vapor transmittance and an excellent dimensional stability, in

spite of reduced thickness of the film, and which is useful

for a polarizing plate protective film.

Next, the compound represented by formula (1) will be

explained in detail.

In formula (1) above, the divalent organic group Y is

an ester bond or a divalent organic group containing an ester

bond. The ester bond herein referred to implies $-C(=O)O-$.

The divalent organic group containing an ester bond

represented by Y represents $-R^1C(=O)O-$; $-C(=O)OR^2-$; $-C(=O)O-$

$R^3-OC(=O)-$; or $-OC(=O)-R^4-C(=O)O-$, in which R^1 and R^2

independently represent a substituted or unsubstituted

alkylene group, and R^3 and R^4 independently represent a

substituted or unsubstituted alkylene group, or $-(R^5O)_pR^5-$, in

which R^5 represents a substituted or unsubstituted alkylene

group, and p is an integer of from 1 to 3. Examples of the

unsubstituted alkylene group represented by R^1, R^2, R^3, R^4 or

R^5 include methylene, ethylene, trimethylene, propylene,

tetramethylene, butylene, pentamethylene, or pentylene.

Examples of the substituted alkylene group represented by R^1,

R^2, R^3, R^4 or R^5 include methylene, ethylene, trimethylene,

propylene, tetramethylene, butylene, pentamethylene or

pentylene, each having methyl, ethyl, n- or iso-propyl, n-,

iso-, or tert-butyl, acetoxy, phenylcarbonyloxy,

cyclohexylcarbonyloxy, phenylcarbonyloxymethyl or

cyclohexylcarbonyloxymethyl as a substituent. The

phenylcarbonyloxy, cyclohexylcarbonyloxy,

phenylcarbonyloxymethyl or cyclohexylcarbonyloxymethyl may

further have a substituent.

Ra and Rb independently represent an alkyl group,

RcC(=O)O- or -C(=O)ORc in which Rc represents a substituted

or unsubstituted phenyl group or a substituted or

unsubstituted cyclohexyl group, and m and n independently

represent an integer of 0 to 5. When m or n is not less than

2, plural Ras or Rbs may be the same or different. Examples

of the alkyl group of Ra and Rb, or examples of the

substituent of the substituted phenyl or cyclohexyl group of

Rc include methyl, ethyl, n- or iso-propyl, or n-, iso-, or

tert-butyl.

In the invention, it is preferred in the invention that

the cyclohexane ring of formula (1) has a substituent (i.e.,

n is preferably an integer of 1 to 5).

In the invention, it is preferred in providing a good

compatibility with the cellulose ester that the cyclohexane

ring of formula (1) has at least one substituent, and the

substituent is preferably an alkyl group.

In formula (1), it is especially preferred that Ra is RcC(=O)O- or -C(=O)ORc in which Rc represents a cyclohexyl group, and m represents an integer of 1 to 5.

In the invention, the content of the compound represented by formula (1) above in the cellulose ester film is from 1 to 30% by weight, preferably from 5 to 25% by weight, and more preferably from 10 to 20% by weight.

Next, the compound having a chemical structure represented by formula (1') will be explained in detail.

The compound has a chemical structure in which the cyclohexane ring and the aromatic ring are connected through a divalent organic group Y'. The divalent organic group is not specifically limited, but preferably has an ester bond. The cyclohexane ring and the aromatic ring may have a substituent. The substituent is not specifically limited, but is preferably an alkyl group. It is preferred in the invention that the cyclohexane ring has a substituent.

It is especially preferred in providing a good compatibility with the cellulose ester that the cyclohexane ring has at least one substituent other than hydrogen, and the substituent is preferably an alkyl group.

The compound having a chemical structure represented by formula (1') has at least one of the chemical structure in
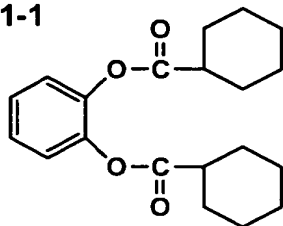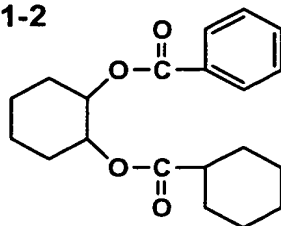
which the cyclohexane ring and the aromatic ring are
connected through the divalent organic group. When the
compound has two or more of the chemical structure, it is
preferably a compound having a structure in which two or more
of the aromatic ring are connected to the cyclohexane ring,
or it may be a compound having a structure in which two or
more of the cyclohexane ring are connected to the aromatic
ring.

In the invention, the content of the compound having a
chemical structure represented by formula (1') above in the
cellulose ester film is from 1 to 30% by weight, preferably
from 5 to 25% by weight, and more preferably from 10 to 20%
by weight.

Examples of the compound represented by formula (1) or
formula (1') will be shown below, but are not limited
thereto. These compounds can be also used as a mixture of
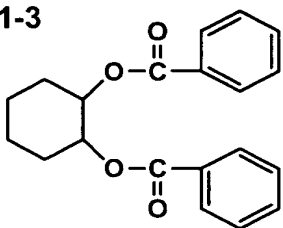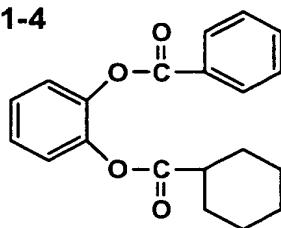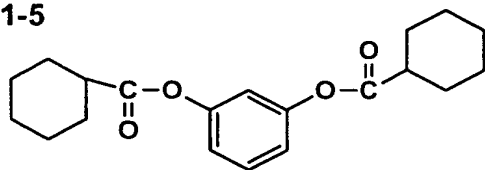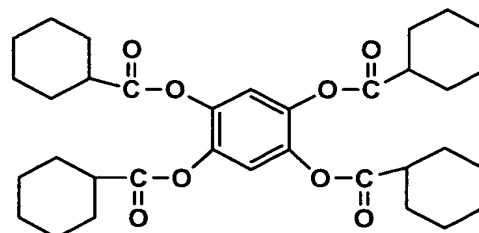two or more kinds thereof.

1-1

1-2

1-3

1-4

1-5

1-6

1--7

1-8

1-9

1-10

1-11

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1-46   **1-47**

1-48

1-49

Of the compounds above exemplified, compounds 1-12, 1-14, 1-16, and 1-30 are preferable. The compound represented by formula (1) or the compound represented by formula (1') has a molecular weight of preferably from 200 to 2000, more preferably from 300 to 1500, still more preferably from 350 to 1000, and most preferably from 350 to 500.

The cellulose ester film comprising the compound represented by formula (1) in an amount of 1 to 30% by weight or the cellulose ester film comprising the compound having a chemical structure represented by formula (1') in an amount of 1 to 30% by weight has the advantageous effects in that it provides a good moisture vapor transmittance and an excellent dimensional stability, in spite of reduced thickness of the film. Such a cellulose ester film also has the advantageous effects in that it provides excellent resistance to UV light or to heat and humidity, which is useful for a polarizing plate protective film.

The compound is available on the market, and can be synthesized according to a conventional synthetic method such as a synthetic method employing an esterification reaction.

The preferable film forming process for manufacturing the cellulose ester film of the invention comprises the steps of a dissolution process, a casting process, a solvent evaporation process, a peeling process, a drying process, and a winding process. Each process will be explained below.
(Dissolution process)

In the invention, a cellulose ester solution also refers to a cellulose ester dope or simply a dope. The dissolution process is one in which cellulose ester in the

flake form is dissolved, while stirring, in organic solvents

mainly comprised of good solvents described later for the

cellulose ester in a dissolution vessel to prepare a dope.

In the invention, the solid content of the dope is

preferably not less than 15% by weight, and more preferably

from 18 to 35% by weight.

The solid content of the dope is preferably not more

than 35% by weight, since a too high solid content of the

dope results in too high viscosity, and may form a shark skin

surface in the cast web to lower flatness of the finished

cellulose ester film.

The viscosity of the dope is preferably adjusted to

from 10 to 50 Pa·s.

In order to carry out said dissolution, there are

various methods such as a method in which dissolution is

carried out at a normal atmospheric pressure, a method in

which dissolution is carried out at a temperature lower than

the boiling point of the preferable organic solvent (i.e., a

good solvent), a method in which dissolution is carried out

at a temperature higher than the boiling point of the good

solvent under increased pressure, a cooling dissolution

method, a method in which dissolution is carried out at a

high pressure, and the like. A method in which dissolution

is carried out at a temperature higher than the boiling point

of the good solvent, for example, 40.4 to 120° C and at

increased pressure, for example, 0.11 to 1.50 Mpa, under the

pressure of which the good solvent is not evaporated, makes

it possible to carry out a rapid dissolution and to minimize

occurrence of foams in the dope.

The cellulose ester used in the invention is preferably

a lower fatty acid ester of cellulose.

The lower fatty acid used in preparation of the lower

fatty acid ester of cellulose implies a fatty acid having a

carbon atom number of not more than 6. Examples of the lower

fatty acid ester of cellulose include cellulose acetate,

cellulose propionate, cellulose butyrate, and a mixed fatty

acid ester of cellulose such as cellulose acetate propionate,

or cellulose acetate butyrate as disclosed in Japanese Patent

O.P.I. Publication Nos. 10-45804 and 8-231761 and US Patent

No. 2,319,052.

The total acyl substitution degree in the cellulose

ester is especially preferably 2.55 to 2.85.

The acyl substitution degree of the cellulose ester can

be measured according to ASTM-D-817-96.

        Among the cellulose esters, cellulose acetate and

cellulose acetate propionate are preferably used. The

polymerization degree of the cellulose ester used in

cellulose ester film of the invention is preferably from 250

to 400, in view of strength of the film.

        The total acyl substitution degree of the cellulose

ester used in the cellulose ester film of the invention is

preferably 2.5 to 3.0, and more preferably 2.55 to 2.85. The

total acyl substitution degree of not less than 2.55 is

preferable in increasing mechanical strength of the cellulose

ester film comprising the compound represented by formula

(1), and the total acyl substitution degree of not more than

2.85 is preferable in increasing dissolution of the cellulose

ester in an organic solvent, and in minimizing occurrence of

foams in the cellulose ester dope.

        In the cellulose acetate propionate, one is preferred

which satisfies the following relationship:

        $2.55 \leqq X + Y \leqq 2.85$

        $1.5 \leqq X \leqq 2.4$

wherein X represents an acetyl substitution degree, and Y

represents a propionyl substitution degree.

In the invention, cellulose esters, which are
synthesized from cotton lint, a tree pulp or other raw
materials, can be used singly or in combination.

The solvent used for preparing a cellulose ester dope
may be any solvent as long as it can dissolve cellulose
esters. Even a solvent, which does not dissolve cellulose
esters, can be used if its mixture with another solvent
dissolves cellulose esters. A mixed solvent, containing a
poor solvent in an amount of 4 to 30% by weight and methylene
chloride as a good solvent, is preferably used.

Examples of good solvents of the cellulose ester
include methylene chloride, methyl acetate, ethyl acetate,
amyl acetate, acetone, tetrahydrofuran, 1,3-dioxolane, 1,4-
dioxane, cyclohexanone, ethyl formate, 2,2,2-
trifluoroethanol, 2,2,3,3-tetrafluoro-1-propanol, 1,3-
difluoro-2-propanol, 1,1,1,3,3,3-hexafluoro-2-methyl-2-
propanol, 1,1,1,3,3,3-hexafluoro-2-propanol, 2,2,3,3,3-
pentafluoro-1-propanol, and nitroethane. Of these, a
halogenated organic compound such as methylene chloride,
dioxolane derivatives, methyl acetate, and ethyl acetate are
preferred. Methylene chloride is especially preferred in
minimizing curl of the cellulose ester film.

Examples of poor solvents include an alcohol having a carbon atom number of 1 to 8, for example, methanol, ethanol, n-propanol, iso-propanol, n-butanol, sec-butanol, or tert-butanol; methyl ethyl ketone; methyl isobutyl ketone; ethyl acetate; propyl acetate; monochlorobenzene; benzene; cyclohexane; tetrahydrofuran; methylcellosolve; and ethylene glycol monomethyl ether. These poor solvents can be used singly or in combination.

As a method of dissolving the cellulose ester in an organic solvent in the manufacture of the cellulose ester film of the invention, a cooling dissolution method is preferable. The cooling dissolution methods include the method disclosed in Japanese Patent O.P.I. Publication Nos. 9-95538, 9-95544, or 9-95557. The dissolution method carried out at a high pressure, disclosed in Japanese Patent O.P.I. Publication Nos. 11-21379, can be also preferably used.

After the dissolution, the cellulose ester solution (dope) is filtered employing filter materials, is then defoamed, and is subsequently pumped to the next process. In the dissolution, a plasticizer, an anti-oxidant, a UV absorbent, a colorant, or fine particles are preferably added to the dope.

These additives may be mixed with cellulose ester or solvents to prepare a cellulose ester dope, or may be added to the cellulose ester dope while or after the dope is prepared.

A plasticizer can be added to the cellulose ester film of the invention. The plasticizer can be used together with the compound represented by formula (1).

The plasticizers used in the invention include a phosphate plasticizer, a phthalate plasticizer, a glycolic acid ester, and citric acid ester plasticizer, but the invention is not limited thereto. Examples of the plasticizer include a phosphate plasticizer such as triphenyl phosphate, tricresyl phosphate, cresyldiphenyl phosphate, octyldiphenyl phosphate, diphenylbiphenyl phosphate, trioctyl phosphate, or tributyl phosphate; a phthalate plasticizer such as diethyl phthalate, dimethoxyethyl phthalate, dimethyl phthalate, dioctyl phthalate, dibutyl phthalate, di-2-ethylhexyl phthalate, butylbenzyl phthalate or dibenzyl phthalate; a glycolic acid ester such as butyl phthalyl butyl glycolate, ethyl phthalyl ethyl glycolate or methyl phthalyl ethyl glycolate; and a citric acid ester plasticizer such as triethyl citrate, tri-n-butyl citrate, acetyltriethyl

citrate, acetyl-tri-n-butyl citrate, or acetyl-tri-n-(2-ethylhexyl) citrate.

These plasticizers may be used singly or in combination. These plasticizers are optionally used as a mixture of two or more kinds thereof. The plasticizer content of the cellulose ester film is preferably 1 to 30% by weight, more preferably 2 to 25% by weight, still more preferably 2 to 15% by weight, and most preferably 3 to 12% by weight.

The cellulose ester film of the invention may contain an additive having the same effect as the plasticizer in addition to the plasticizer. These additives can provide the effects of the invention which the plasticizer provides as long as they are lower molecular weight organic compounds capable of plasticizing the cellulose ester film. These organic compounds are not added to the cellulose ester film for the purpose of plasticizing the film, but can provide the same effects as the plasticizer depending upon the addition amount thereof.

The cellulose ester film of the invention preferably contains a UV absorbent. The UV absorbent in the invention is preferably a UV absorbent which has excellent absorption of ultraviolet light having a wavelength of 370 nm or less,

and has reduced absorption of visible light having a
wavelength of 400 nm or more in clearly providing a liquid
crystal image. The UV absorbents have a transmittance at 370
nm of preferably not more than 10%, more preferably not more
than 5%, and most preferably not more than 1%.

The UV absorbents used in the invention are not
specifically limited, but they include an oxybenzophenone
compound, a benzotriazole compound, a salicylic acid ester
compound, a benzophenone compound, a cyanoacrylate compound
and a nickel complex compound.

As UV absorbents preferably used in the invention, the
benzotriazole or benzophenone type UV absorbent is preferably
used which has high transparency, and minimizes deterioration
of a polarizing plate or a liquid crystal. The benzotriazole
type UV absorbent is especially preferably used, since it
minimizes undesired coloration.

The UV absorbents added to the cellulose ester film of
the invention are preferably UV absorbents having a
distribution coefficient of not less than 8.5. The UV
absorbents having a distribution coefficient of not less than
8.5 have the effect lowering a moisture vapor permeation.
The distribution coefficient of the UV absorbents is more
preferably not less than 9.0, and still more preferably not

less than 10.0. The UV absorbents are preferably UV

absorbents containing no halogens in the molecules.

Examples of the UV absorbents preferably used in the

invention will be shown below, but the invention is not

limited thereto.

UV absorbents	R_1	R_2	R_3	Distribution coefficient
UV-1	tert—C_4H_9	$CH_2CH_2COOC_8H_{17}$	Cl	10.0
UV-2	$C_{12}H_{25}$	CH_3	Cl	10.0<
UV-3	tert—C_4H_9	tert—C_4H_9	Cl	9.1
UV-4	tert—C_5H_{11}	tert—C_5H_{11}	H	9.0
UV-5	tert—C_4H_9	CH_3	Cl	8.6
UV-6	tert—C_4H_9	tert—C_4H_9	H	8.4

The distribution coefficient expresses the distribution

factor of octanol and water defined by the following formula:

Distribution coefficient = Log Po/w, Po/w = So/Sw

So: solubility of a UV absorbent in n-octanol at 25 °C

Sw: solubility of the UV absorber in pure water at 25 °C

The distribution coefficient can be measured employing

n-octanol as well as water. However, in the present

invention, the distribution coefficient is obtained employing

a calculation method according to HPLC. This method employs

a high speed chromatography, which is described in an OECD

Guideline 117 distribution coefficient (n-octanol/water) high

speed chromatography (adopted on March 30, 1989).

Measurement conditions in HPLC are described below.

Apparatus: LC module (manufactured by Waters Co., Ltd.)

Column: Inertsil ODS-2 250 mm × 4.6 mm (manufactured by GL

Science Co., Ltd.)

Temperature: 40° C

Eluent: methanol:a 1% aqueous phosphoric acid solution

= 90:10

Flow rate: 1.0 ml/minute

Detection wavelength: 210 nm

Injected sample: an approximately 50 ppm methanol solution

The UV absorbents can be used singly or as a mixture of

two or more kinds thereof. The UV absorbent content of the

cellulose ester film is different depending on kinds of UV

absorbents used or usage conditions, but is preferably 0.2 to

5 g per m^2 of cellulose ester film, and more preferably 0.4

to 2 g per m^2 of cellulose ester film.

In the invention, an additive such as a blue dye may be used in order to adjust the hue of the film. The prefereed dyes include anthraquinone dyes. The anthraquinone dyes can have any substituent at the 1- to 8- positions of their chemical structures. The preferred substituents include an anilino group, a hydroxy group, an amino group, a nitro group or hydrogen. The content of the dyes in the cellulose ester film is preferably 0.1 to 1000 $\mu g/m^2$, and more preferably 10 to 100 $\mu g/m^2$ in order to maintain the transparency of the film.

The cellulose ester film of the invention preferably contains particles as a matting agent in order to give a good slip property to the film. The particles were preferably surface treated with an organic compound in giving a reduced haze to the film.

Examples of the organic compound used in the surface treatment include halogenated silanes, alkoxysilanes, silazanes, and siloxanes.

Particles having a larger average particle diameter have a high matting effect, and particles having a smaller average particle diameter have a good transparency. The primary particles of the particles have an average primary

particle size of preferably 5 to 50 nm, and more preferably 7
to 20 nm.

The particles used are not specifically limited.
Examples of the particles include Aerosil 200, 200V, 300,
R972, R972V, R974, R202, R812, OX50, or TT600 (each produced
by Nihon Aerosil Co., Ltd.), and Aerosil 200V and R972V are
preferred.

These particles ordinarily form secondary particles
having an average particle size of 0.01 to 1.0 μm, and exist
as aggregates in the cellulose ester film to form a film
surface having a peak to valley distance of 0.01 to 1.0 μm.
The particle content of the cellulose ester film is
preferably 0.005 to 0.3% by weight.

The cellulose ester film of the invention preferably
contains silicon dioxide particles, and a cellulose ester
film is especially preferred which is prepared employing a
cellulose ester dope containing the silicon dioxide particles
and a UV absorbent having a distribution coefficient of not
less than 8.5, according to a solution cast film manufacture
method, since foreign matter, which occurs due to aggregation
of the particles in the cellulose ester dope, is minimized.

As the methods of preparing a cellulose ester dope
containing a dispersion of the particles as described above,
the following three are exemplified.

(Method A)

A solvent and the particles are mixed in a disperser
with stirring, and dispersed to obtain a dispersion of the
particles. The dispersion is added to a cellulose ester
dope, and stirred.

(Method B)

A solvent and the particles are mixed in a disperser
with stirring, and dispersed to obtain a dispersion of the
particles. Separately, a small amount of cellulose ester is
dissolved in a solvent with stirring, and added with the
above dispersion to obtain a particle addition solution. The
resulting particle addition solution is mixed with a
cellulose ester dope in an in-line mixer.

(Method C)

A small amount of cellulose ester is dissolved in a
solvent with stirring, added with particles, and dispersed in
a disperser to obtain a particle addition solution. The
resulting particle addition solution is mixed with a
cellulose ester dope in an in-line mixer.

The method A is preferred in that silicon dioxide particles are effectively dispersed in a solvent, and the method C is preferred in that dispersed silicon dioxide particles in a solvent are difficult to be re-aggregated. The method B is more preferred both in that silicon dioxide particles are effectively dispersed in a solvent, and in that dispersed silicon dioxide particles in a solvent are difficult to be re-aggregated.

(Dispersion method)

When silicon dioxide particles are dispersed in a solvent to obtain a silicon dioxide dispersion, the silicon dioxide concentration of the dispersion is preferably 5 to 30% by weight, more preferably 10 to 25% by weight, and most preferably 15 to 20% by weight. The higher concentration of the particles tends to lower the turbidity of the dispersion, lowers haze, and minimizes occurrence of aggregates, which is preferable.

The organic solvents used in the dispersion include lower alcohols. Examples of the lower alcohols include methyl alcohol, ethyl alcohol, propyl alcohol, and butyl alcohol. Solvents other than the lower alcohols are not specifically limited, and solvents used in the preparation of the cellulose ester dope are preferred.

Employing the cellulose ester dope obtained above, a cellulose ester film can be prepared through a dope cast process explained below.

(Casting process)

The casting process is one in which a dope is conveyed to a pressure die through a pressure type metering gear pump, and cast from said pressure die on a support (hereinafter referred to also as a support) for casting such as a moving endless metal belt or a rotating metal drum at a casting position. The surface of the support for casting is specular.

As other casting processes, there is a doctor blade method adjusting the dope thickness of the cast dope with a doctor blade or a reverse roller method adjusting the dope thickness of the cast dope with a reverse roller coater rotating reversely. A pressure die is preferred in which the slit shape at the mouth piece portion can be regulated and the film thickness is readily regulated to be uniform. Examples of the pressure die include a coat hanger die, a "T" die, and the like, and any of these is preferably employed.

In order to increase the casting speed, two or more pressure dies may be provided on the metal support and dopes divided into two or more may be simultaneously cast on the

metal support. A laminated cellulose ester film can be prepared by simultaneously casting (co-casting) plural cellulose ester dopes different in composition from a die with plural slits on a support.

A cellulose ester film is prepared by casting the cellulose ester dope obtained above on a support such as a belt or a drum. In the invention, a solution cast film manufacture process employing a belt is especially preferred. This is because drying conditions on the support can be easily controlled in detail.

(Solvent evaporation process)

The solvent evaporation process is one in which a web (in the invention, a film is called a web which is formed after a dope is cast on a support for casting) is heated on a support for casting and solvents are evaporated. In order to evaporate solvents, methods include a method in which air is blown from the web side, and/or a method in which heating is carried out from the reverse surface of the support employing liquid, and a method in which heating is carried out from the surface as well as the revere surface employing heat radiation. Of these, the reverse surface liquid heating method is preferred due to high drying efficiency. Further, these methods are preferably combined. The cast web on the

support is dried preferably on the support at 40 to 100° C.
Heating the web to a temperature of 40 to 100° C is
preferably carried out employing air having that temperature
or an infrared ray heater.

In the invention, the web is preferably peeled within
the time range of from 30 to 90 seconds after the casting on
the support in view of peeling property, film surface
quality, moisture vapor permeability and film curl.

The peeling process is one in which a web, which has
been subjected to evaporation of solvents on the support, is
peeled at the peeling position. The peeled web is conveyed
to the subsequent process. When the residual solvent amount
(represented by the formula described below) is too large, it
may be difficult to peel the web. On the contrary, when
peeling is carried out after fully drying the web on the
support, a part of the web may peel prior to the peeling
position.

It is preferred in the invention that temperature at
the peeling position on the support is 10 to 40° C, and
preferably 11 to 30° C. The residual solvent amount at the
peeling position is preferably 25 to 120% by weight, and more
preferably 40 to 100% by weight.

The residual solvent amount in the invention is expressed employing the following formula:

Residual solvent amount (weight %) = {(weight of a web before heat treatment - weight of a web after heat treatment)/weight of a web before heat treatment} × 100

wherein the heat treatment represents heating the web at 115° C for one hour.

In order to adjust the residual solvent to the amount described above at the peeling position, the temperature of the support at the peeling position is preferably set at the range described above so that evaporation of the organic solvent from the web was effectively carried out by controlling the temperature of the surface of the support for casting. In order to control the temperature of the support, a heat transfer method having a good efficiency of heat transfer, for example, heat transfer from the rear surface of the support, is preferred.

A heat transfer employing radiant heat or a hot air is difficult to control the temperature of the support, and is not so preferable. When the support is a rotating belt, and is at the lower position, the temperature of the belt can be controlled by mildly blowing the hot air onto the support.

The support temperature can be varied at the different

positions of the support through different heating methods,

and can be varied at the casting position on the support, at

the drying position on the support, or at the peeling

position on the support.

Listed as a method to increase the film forming speed

is a gel casting method (in which peeling can be carried out

even though the amount of residual solvents is relatively

great).

The gel casting methods include a method in which poor

solvents with respect to the cellulose ester are added to a

dope and gelling is carried out after casting said dope, and

also a method in which gelling is carried out by decreasing

the temperature of a support, and the like. There is further

a method in which metal salts are added to the cellulose

ester dope.

By strengthening the web through gelling the dope on

the support, it is possible to carry out earlier peeling and

to increase the casting speed.

When the peeling is carried out at the time when the

residual solvent amount is still relatively great, the web

may be too soft, in which during peeling, the flatness of the

web tends to be degraded, and wrinkles and longitudinal

streaks due to the peeling tension tend to be formed. Accordingly, the residual solvent amount at the peeling is determined so that productivity and quality are balanced. The web is ordinarily peeled from the support at a peel tension of 196 to 245 N/m. When wrinkles easily occur, the peel tension is preferably not more than 190 N/m, more preferably from a possible lowest peel tension to 166.6 N/m, still more preferably from a possible lowest peel tension to 137.2 N/m, and most preferably from a possible lowest peel tension to 100 N/m. Less peel tension is preferred, since a retardation in plane R_0 can be maintained lower. The retardation in plane R_0 is preferably less than 20 nm, more preferably less than 10 nm, still more preferably less than 5 nm, and most preferably from 0 to 1 nm.

In the invention, a retardation in plane R_0 of a cellulose ester film can be computed from refractive indices at a wavelength 590 nm in the three axis directions, nx, ny, and nz of the film obtained by being measured by means of an automatic birefringence meter KOBRA-21ADH (produced by Oji Keisokukiki Co., Ltd.). The retardation in the thickness direction Rt of the film is preferably 0 to 300 nm, more preferably 0 to 150 nm, and most preferably 0 to 70 nm.

$R_0 = (nx - ny) \times d$

Rt = {(nx + ny)/2-nz} x d

The cellulose ester film of the invention satisfies preferably the following formula between a retardation in plane R_0 and an angle θ (radian) of the delayed phase axis direction with respect to the mechanical direction, and such a cellulose ester film is preferably used as an optical film such as a protective film of a polarizing plate.

P $\leqq$ 1 - $\sin^2(2\theta)$ $\sin^2(\pi R_0/\lambda)$

P = 0.9999

In the above formula, nx represents the refractive index in the delayed phase axis direction in the plane of the film, ny represents the refractive index in the advanced phase axis direction in the plane of the film, nz represents the refractive index in the thickness direction of the film, d represents the film thickness (nm), θ represents the angle (radian) of the delayed phase axis direction in the plane of the film with respect to the mechanical direction of the film, λ represents the wavelength 590 nm of light used for measuring the above nx, ny, nz, and θ, and π represents the circle ratio.

(Drying process)

The drying process is a process, which dries the web employing a drying apparatus in which said web is alternatively transported through staggered rollers and/or a tenter apparatus in which said web is transported while holding both edges of the web employing clips. In the drying process, a transport tension for transporting the web is preferably the possible lowest, since R_0 can be maintained lower. The transport tension is preferably not more than 190 N/m, more preferably not more than 170 N/m, still more preferably not more than 140 N/m, and most preferably from 100 to 130 N/m. It is especially effective that the transport tension is maintained within the above range till the residual solvent amount is not more than 5% by weight.

A common drying method is one in which both surfaces of the web are heated by heated air flow. Instead of the air flow, employed is a method in which heating is carried out employing microwaves. Too rapid drying tends to degrade the flatness of the finished film. A high temperature drying is preferably applied to the web having a residual solvent content of not more than 8% by weight. During the entire drying process, drying temperature is commonly from 40 to 250° C, and preferably 40 to 160° C.

In the drying process after peeling the web from the
support, the web tends to shrink in the transverse direction
due to evaporation of the organic solvent. When the web is
dried rapidly at a higher temperature, the tendency of the
web shrinkage is stronger.

Drying of the web while the shrinkage is minimized as
far as possible is preferable in improving a flatness of the
finished cellulose ester film. In view of the above, a
method disclosed in Japanese Patent O.P.I. Publication No.
62-46625 is preferably used which comprises drying the web
while holding the both edges in the transverse direction of
the web by clips or pins to maintain the web width (called "a
tenter method"). A tenter method employing clips or a pin-
tenter method employing pins is preferably used.

Drying the web while maintaining the web width can
provide a cellulose ester film in which a retardation in
plane Ro of the film is reduced. In this case, the
stretching magnification factor in the transverse direction
of the web is preferably from 1.00 to 1.15, and more
preferably from 1.01 to 1.1. It is preferred in the tenter
method that the residual solvent of the web at initial tenter
stage is from 20 to 70% by weight, and drying is carried out

until the residual solvent of the web is not more than 10% by weight, and preferably not more than 5% by weight.

When the cellulose ester film of the invention is used as a phase difference film, the web containing the residual solvent at the peeling can be stretched in the transverse direction and/or in the mechanical direction by a factor of from 1.01 to 2.5. In this case, the web is stretched by a factor of preferably from 1.15 to 1.6, which can provide a cellulose ester film having an R_0 of from 20 to 1000 nm.

The cellulose ester film peeled from the support is further dried in the drying process to give a residual solvent content in the film of preferably not more than 0.5 weight %, more preferably not more than 0.1 weight %, and most preferably from 0 to 0.01 weight %.

In the drying process of the film, the film is generally transporting on rollers or in the above pintenter while drying. The film for a liquid crystal display is preferably dried maintaining the film width in the pintenter, which increases dimensional stability of the film. It is especially preferable in view of increased film dimensional stability that the film is dried while holding the film width of a film immediately after the film is peeled from the support, which still has a relatively high residual solvent

content. The means for drying the film is not specifically limited, and heated air, infrared light, heated rollers or micro waves are generally employed. The heated air is preferably used in view of its convenience. It is preferable that the drying temperature is gradually elevated in separate 3 to 5 stages in the range of from 40 to 150° C. It is more preferable in view of film dimensional stability that the drying temperature is gradually elevated in separate 3 to 5 stages in the range of from 80 to 140° C.

In the process from the casting to the drying in the solution cast film manufacture process, drying of the web in the drying apparatus may be carried out at an air atmosphere or at an atmosphere of an inert gas such as a nitrogen gas, a carbon dioxide gas or an argon gas.

It is not needless to say that the explosion limits of the vaporized organic solvents in the drying apparatus should be always considered.

(Winding process)

This process is one in which after the residual solvent content of the web is not more than 2% by weight, the resulting cellulose ester film is wound around a spool. The cellulose ester film having a residual solvent content of not more than 0.4% by weight provides good dimensional stability.

Any of conventional winding methods can be used, and examples of the winding methods include a constant torque method, a constant tension method, a taper tension method, and a method programmed so as to have a constant inside stress.

The thickness of the cellulose ester film can be adjusted by controlling a dope concentration, a dope amount supplied by a pump, a slit width of the mouth piece portion of a die, an extrusion pressure of a die, or a moving speed of a support for casting.

It is preferred that the thickness of the cellulose ester film is uniformly regulated by feeding back a thickness information detected by a thickness detector to the devices described above through a system programmed in advance for information to be fed back to them.

The optimum thickness of the cellulose ester film is different depending upon purpose of use. The thickness of the cellulose ester film is ordinarily from 5 to 500 μm, and preferably from 10 to 200 μm. The thickness of a cellulose ester film used in a liquid crystal display is from 10 to 120 μm. The cellulose ester film of the invention has a good moisture vapor transmittance, and excellent dimensional

stability, even when it has a reduced thickness of 10 to 60 μm.

In the invention, moisture vapor transmittance of the film was measured at $25\pm0.5°$ C and $90\pm2\%$ RH (condition A) according to a method described in JIS Z 0208. The moisture vapor transmittance of the film is preferably from 20 to 250 $g/m^2\cdot24$ hours, and more preferably 25 to 250 $g/m^2\cdot24$ hours. The above range of the moisture vapor transmittance is preferred in view of durability of a polarizing plate employing the film or drying of an adhesive used in the manufacture of a polarizing plate employing the film.

Dimensional stability of the cellulose ester film of the invention can be improved by reducing the weight change of the film after storage at 80° C and at 90% RH.

The cellulose ester film of the invention has rate of weight change within the range of preferably $\pm2\%$, the rate representing, in terms of percentage, the ratio of the difference between the film weights before and after storage at 80° C and 90% RH for 48 hours to the film weight before the storage. Such a cellulose ester film, even when it has a reduced thickness, provides an excellent dimensional stability as well as improved moisture vapor permeability.

After the cellulose ester film of the invention is stored at 80° C and at 90% RH for 48 hours, rate of dimensional change in the mechanical direction (MD) of the film and rate of dimensional change in the transverse direction (TD) of the film both are preferably within the range of ± 0.5%, more preferably within the range of ± 0.3%, still more preferably within the range of ± 0.1%, and most preferably within the range of ± 0.05%.

The rate of dimensional change referred to in the invention is a characteristic value showing dimensional change in the mechanical and transverse directions of the film after stored under severe conditions such as high temperature and high humidity. Typically, after the film is stored at high temperature, at high humidity or at high temperature and high humidity, dimensional change in the mechanical and transverse directions of the film is measured.

A film sample for test was cut into a size of 150 mm (in the transverse direction) x 120 mm (in the mechanical direction), and two points 100 mm distant from each other were marked with the cross "+" on the film surface in each of the mechanical direction (MD) and the transverse direction (TD), employing a knife. The resulting sample was subjected to humidity conditioning at 23° C and at 55% RH for 24 hours,

and the distances L1 in the mechanical and transverse

directions between the two points before high temperature and

high humidity treatment was measured through a factory

microscope. Thereafter, the sample was subjected to high

temperature and high humidity (at 80° C and at 90% RH for 48

hours), and then again subjected to humidity conditioning at

23° C and at 55% RH for 24 hours. The distances L2 in the

mechanical and transverse directions between the two points

after the treatment were measured through a factory

microscope. The rate of dimensional change is represented by

the following formula:

Rate (%) of dimensional change = $\{(L2-L1)/L1\}$ x 100

wherein L1 represents the distance before the treatment

between the two points, and L2 represents the distance after

the treatment between the two points.

Intended dimensional change of the film can be measured

by marking two points on the film surface in each of the

transverse and mechanical directions

After the cellulose ester film is stored at 105° C for

5 hours, the rate of dimensional change in the MD direction

and the rate of dimensional change in the TD direction both

fall within the range of preferably ±0.5%, more preferably

±0.3%, still more preferably ±0.1%, and most preferably

±0.05%.

In the cellulose ester film of the invention, tensile

stress in the MD direction of the film and tensile stress in

the TD direction of the film both are preferably from 90 to

170 N/mm^2, and more preferably from 120 to 160 N/mm^2.

The moisture content of the cellulose ester film is

preferably from 0.1 to 5%, more preferably from 0.3 to 4%,

and most preferably from 0.5 to 2%.

The cellulose ester film of the invention has a

transmittance of preferably not less than 90%, more

preferably not less than 92%, and most preferably not less

than 93%. The cellulose ester film of the invention has a

haze of preferably not more than 0.5, more preferably not

more than 0.1%, and most preferably 0%.

The absolute curl value of the cellulose ester film of

the invention is preferably lower. The film curl can be in

the + direction or in the - direction. The absolute curl

value of the cellulose ester film is preferably not more than

30, more preferably not more than 20, and most preferably not

more than 10. The curl value is represented in terms of

radius of curvature (1/m).

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The process of manufacturing the cellulose ester film of the invention according to a solution cast film manufacture method will be explained below employing figures.

Fig. 1 is a schematic view showing one of preferred embodiments of a solution cast film manufacture process. Fig. 1(a) is a schematic view showing a process which comprises a dope casting step, and a roller transporting and drying step in that order. Fig. 1(b) is a schematic view showing a process which comprises a dope casting step, a roller transporting and drying step, and a tenter transporting and drying step in that order. Fig. 1(c) is a schematic view showing a process which comprises a dope casting step, a tenter transporting and drying step, and a roller transporting and drying step in that order. Fig. 1(d) is a schematic view showing a process which comprises a dope casting step, a first roller transporting and drying step, a tenter transporting and drying step, and a second roller transporting and drying step in that order.

In the invention, the process comprising a tenter transporting and drying step or a roller transporting and drying step is a process which resides between a web peeling step and a web winding step, during which elongation or shrinkage of the web is regulated. The tenter transporting

and drying step refers to a step of drying a cellulose ester web while transporting the web in a tenter, during which elongation or shrinkage of the web is regulated. The roller transporting and drying step refers to a step of drying a cellulose ester web while transporting the web through rollers, during which elongation or shrinkage of the web is regulated.

In Figs. 1(a) through 1(d), numerical number 1 shows an endless moving belt support. As the support is used a mirror surface metal band. Numerical number 2 shows a die for casting on the support 1 a dope in which cellulose ester is dissolved in a solvent. Numerical number 3 shows a peel position at which, after the cast dope is solidified on the support 1 to form a web, the web is peeled from the support 1. Numerical number 4 shows a peeled web. Numerical number 5 shows a tenter transporting and drying step. Numerical number 51 shows an air discharging port, and numerical number 52 shows a drying air introducing port. Air discharging port 51 and the drying air introducing port 52 may be reversed. Numerical number 6 shows a tension changing means. Examples of the tension changing means include nip rollers and suction rollers. The tension changing means may be located between any two adjacent steps.

Numerical number 8 shows a roller transporting and
drying step. Numerical number 81 shows a drying chamber,
numerical number 82 shows an air discharging port, and
numerical number 83 shows a drying air introducing port. The
air discharging port 82 and the drying air introducing port
83 may be reversed. Numerical number 84 shows upper
transporting rollers, and numerical number 85 shows lower
transporting rollers. One upper transporting roller and one
lower transporting roller which immediately follows
constitute one pair of transporting rollers, and transporting
rollers 84 and 85 are composed of plural pairs of
transporting rollers. Numerical number 7 shows a cellulose
ester film winding step at which the cellulose ester film is
wound around a spool to form a roll.

In a process illustrated in Fig. 1(d), the roller
transporting and drying step, which resides upstream of the
tenter transporting and drying step 5, is called a first
roller transporting and drying step, and the roller
transporting and drying step, which resides downstream of the
tenter transporting and drying step 5, is called a second
roller transporting and drying step. A cooling step, which
is not illustrated in any of Fig. 1(a) through Fig. 1(d), may

be optionally provided prior to the cellulose ester film

winding step.

In the invention, a cellulose ester film can be

manufactured according to any solution cast film manufacture

method as described above.

The cellulose ester film of the invention is preferably

used in a member of a liquid crystal display such as a

polarizing plate protective film in view of good moisture

vapor permeation and dimensional stability thereof. The

cellulose ester film of the invention is especially

preferably used in a polarizing plate protective film in

which severe moisture vapor permeation and dimensional

stability both are required.

The polarizing plate in the invention can be prepared

according to conventional methods. There is, for example, a

method in which an optical film or a cellulose ester film is

subjected to an alkali saponification, and the resulting film

is adhered through an aqueous completely saponified polyvinyl

alcohol solution to both surfaces of a polarizing film which

is prepared by immersing a polyvinyl alcohol film in an

iodine solution, and stretching the resulting film. The

alkali saponification refers to treatment in which the

cellulose ester film is immersed in a strong alkali solution

at high temperature in order to enhance wettability of the film to an aqueous adhesive and provide good adhesion to the film.

Various functional layers such as a hard-coat layer, an anti-glare layer, an anti-reflection layer, an anti-stain layer, an anti-static layer, a conductive layer, an optically anisotropic layer, a liquid crystal layer, an orientation layer, a sticky layer, an adhesion layer, and a subbing a sticky layer can be provided on the cellulose ester film of the invention. These functional layers can be provided on the film by coating, evaporation, spattering, plasma CVD or plasma treatment under atmospheric pressure.

The polarizing plate obtained above is provided on both sides or one side of a liquid crystal cell, and the resulting material is installed in a liquid crystal display.

When the cellulose ester film of the invention is used in a polarizing plate protective film, a polarizing plate having a reduced thickness and having excellent durability, dimensional stability and optical isotropy can be obtained. A liquid crystal display, employing the polarizing plate or the phase difference film of the invention, can maintain stable displaying performance for a long term.

The cellulose ester film of the invention is also used for an anti-reflection film or an optical compensation film.

EXAMPLES

The invention will be detailed according to the following examples, but is not limited thereto.

Example 1

1. Preparation of a dope

The dope composition A as shown below was incorporated in a tightly sealed vessel, and stirred at 80° C under increased pressure to prepare a cellulose ester solution. Particles AEROSIL 200V (produced by Nippon Aerosil Co., Ltd.) were dispersed in a part of ethanol to be added, and incorporated in advance in the tightly sealed vessel. The resulting cellulose ester solution was cooled to a temperature at which casting was carried out, allowed to stand, subjected to defoaming treatment, and filtered employing Azumi filter paper No. 244, produced by Azumi Roshi Co., Ltd. Thus, a dope A was prepared. Dopes B through G were prepared in a similar manner as a dope A.

(Measurement of substitution degree of cellulose ester used)

The substitution degree of cellulose ester used was measured according to the method defined in ASTM-D817-96.

(Dope composition A)

Compound 1-14
(a compound falling within formula (1))   15 kg

UV absorbents

UV-1   0.5 kg

UV-2   0.5 kg

UV-5   0.5 kg

Particles AEROSIL 200V
(produced by Nippon Aerosil Co., Ltd.)   0.05 kg

Acetyl cellulose with an acetyl
substitution degree of 2.7   83.5 kg

Methylene chloride   290 l

Ethanol   25 l

(Dope composition B)

Compound 1-30
(a compound falling within formula (1))   15 kg

UV absorbents

UV-1   0.5 kg

UV-2   0.5 kg

UV-5   0.5 kg

Particles AEROSIL 200V
(produced by Nippon Aerosil Co., Ltd.)   0.05 kg

Cellulose acetate propionate with an acetyl
substitution degree of 2.0 and a propionyl
substitution degree of 0.8   83.5 kg

Methylene chloride   265 l

Ethanol   50 l

(Dope composition C)

Compound 1-12
(a compound falling within formula (1))   15 kg

UV absorbents

UV-1   0.5 kg

UV-2   0.5 kg

UV-5   0.5 kg

Particles AEROSIL 200V
(produced by Nippon Aerosil Co., Ltd.)   0.05 kg

Cellulose acetate propionate with an acetyl
substitution degree of 2.0 and a propionyl
substitution degree of 0.8   83.5 kg

Methyl acetate   210 l

Ethanol   90 l

(Dope composition D)

Compound 1-16
(a compound falling within formula (1))   15 kg

UV absorbents

UV-1   0.5 kg

UV-2   0.5 kg

UV-5   0.5 kg

Particles AEROSIL 200V
(produced by Nippon Aerosil Co., Ltd.)   0.05 kg

Triacetyl cellulose with an acetyl
substitution degree of 2.88   83.5 kg

Methylene chloride   290 l

Ethanol   25 l

(Dope composition E)

Compound 1-16
(a compound falling within formula (1))   15 kg

UV absorbents

UV-6   1.5 kg

Particles AEROSIL 200V
(produced by Nippon Aerosil Co., Ltd.)   0.05 kg

Triacetyl cellulose with an acetyl
substitution degree of 2.88   83.5 kg

Methylene chloride   290 l

Ethanol   25 l

(Dope composition F)

Comparative Compound shown later   15 kg

UV absorbents

UV-1   0.5 kg

UV-2   0.5 kg

UV-5   0.5 kg

Particles AEROSIL 200V
(produced by Nippon Aerosil Co., Ltd.)   0.05 kg

Triacetyl cellulose with an acetyl
substitution degree of 2.88   83.5 kg

Methylene chloride   290 l

Ethanol   25 l

(Dope composition G)

Triphenyl phosphate (TPP)   15 kg

UV absorbents

UV-1   0.5 kg

UV-2   0.5 kg

UV-5   0.5 kg

Particles AEROSIL 200V
(produced by Nippon Aerosil Co., Ltd.)   0.05 kg

Triacetyl cellulose with an acetyl
substitution degree of 2.88   83.5 kg

Methylene chloride   290 l

Ethanol   25 l

Comparative Compound

2. Preparation of cellulose ester film

Cellulose ester film was prepared according to the procedures described below employing an apparatus as shown in Fig. (d).

The dope A was uniformly cast at 30° C on an endless stainless steel belt support, which was heated on the rear side with 35° C water, to form a dope film. The dope film

was blown with 45° C air and dried. Thirty minutes after the
casting, the film was peeled from the support, and further
dried while transporting through many rollers. The
temperature at the peel position on the endless stainless
steel belt support was set at 10° C. The peeled film was
further dried while transported for one minute in a first dry
zone set at 50° C, transported for 30 seconds in a second dry
zone set at 90° C, and transported for ten minutes in a third
dry zone set at 115° C. In the second dry zone, the film was
stretched by a factor of 1.05 in the transverse direction by
means of a tenter. The dried film was wound around a spool
to obtain a cellulose ester film in the roll form with a roll
length of 2500 m and with a thickness of 40 μm. The residual
solvent content at the winding of the film was less than
0.01% by weight. Thus, cellulose ester film sample 1 was
prepared.

Cellulose ester film samples 2 through 7 were prepared
in the same manner as in cellulose ester film sample 1,
except that dopes B through G were used, respectively,
instead of dope A. The resulting cellulose ester film
samples are shown in Table 1.

The cellulose ester film samples 1 through 7 were evaluated according to the following methods, and the results are also shown in Table 1.

Evaluation of cellulose ester film samples

(Measurement of retardation R_0)

Refractive indices at wavelength 590 nm in the three axis directions, Nx, Ny, and Nz of each cellulose ester film sample were measured by means of a birefringence meter KOBRA-21ADH (produced by Oji Keisokukiki Co., Ltd.), and retardation Ro was computed according to the following formula.

$$R_0 = (Nx - Ny) \times d$$

wherein Nx represents a maximum refractive index in plane of the film, Ny represents a refractive index in plane of the film in the direction normal to that providing Nx, and d represents a thickness (nm) of the film.

(Measurement of rate of dimensional change)

Each sample was cut into a size of 150 mm (in the transverse direction) x 120 mm (in the mechanical direction), and employing a knife, two points 100 mm distant from each other were marked with the cross "+" on the film surface in each of the mechanical direction (MD) and the transverse direction (TD). The resulting sample was subjected to

humidity conditioning at 23° C and at 55% RH for 24 hours,
and the distances L1 in the mechanical and transverse
directions between the two points before high temperature and
high humidity treatment was measured through a factory
microscope. Thereafter, the sample was subjected to high
temperature and high humidity treatment at 80° C and at 90%
RH for 48 hours, and then again subjected to humidity
conditioning at 23° C and at 55% RH for 24 hours. The
distances L2 in the mechanical and transverse directions
between the two points after the treatment were measured
through a factory microscope. The rate of dimensional change
is represented by the following formula:

Rate (%) of dimensional change = $\{(L2-L1)/L1\}$ x 100

wherein L1 represents the distance before the treatment
between the two points, and L2 represents the distance after
the treatment between the two points.

(Moisture vapor transmittance)

Moisture vapor transmittance of the film was measured
at $25\pm0.5°$ C and $90\pm2\%$ RH (condition A) according to a
method described in JIS Z 0208, and represented in terms of a
moisture amount (g), which evaporated from the sample in 24
hours per 1 m^2 of the sample.

(Rate of weight change)

From each sample was cut a 10 X 10 cm^2 film sample. The resulting sample was allowed to stand at 23° C and at 55% RH for 24 hours, and then weighed. Subsequently, the sample was subjected to heat treatment at 80° C and at 90% RH for 48 hours. After the surface of the resulting sample was softly wiped, the sample was again allowed to stand at 23° C and at 55% RH for one day, and then weighed. The rate of weight change is represented by the following formula:

Rate of weight change (%)

= {(Film weight before heat treatment - Film weight after heat treatment)/Film weight before heat treatment} X 100

(Resistance to UV light)

Employing an EYE SUPER UV TESTER TYPE SUV-F1 (produced by IWASAKI ELECTRIC Co., LTD.), each sample was subjected to UV irradiation of 1500 mW/cm^2 for 96 hours through a metal halide lamp. After the irradiation, change of hue of the sample was observed, and a test of folding the sample into two parts was carried out. The sample was evaluated according to the following criteria.

A: Neither discoloration of the hue nor breakage due to folding after UV irradiation was observed.

B: Both discoloration of the hue and breakage due to folding

after UV irradiation were observed.

(Measurement of curl value)

Each cellulose ester film sample was stored at 23° C

and 55% RH for 48 hours, and cut into a piece with a size of

2 mm (in the mechanical direction) x 50 mm (in the transverse

direction). The resulting film piece was further subjected

to humidifying treatment at 23 ± 2° C and 55% RH for 24

hours. Thereafter, a circle having an arc equal to the curl

of the resulting piece was determined employing a curvature

scale, and the radius of curvature of the circle was obtained

as the curl value of the cellulose ester film sample.

Foreign matter defects

(Foreign material defects)

The number of foreign materials with a size of not less

than 30 µm per m^2 of each sample was counted.

Table 1

Cellulose ester film sample No.	Kinds of dope	Thickness (μm)	Moisture vapor transmittance (g/m². 24 hr)	Rate of weight change (%)	Rate of dimensional change (%)	Resistance to UV light	R_0 (nm)	Foreign material defects	Curl value (1/m)	Remarks
1	Dope A	40	180	0.1	-0.05	A	0	4	10	Inv.
2	Dope B	40	195	0.1	-0.05	A	1	3	10	Inv.
3	Dope C	40	190	0.1	-0.05	A	1	5	5	Inv.
4	Dope D	40	200	0.2	-0.1	A	2	5	15	Inv.
5	Dope E	40	220	0.2	-0.1	A	2	15	15	Inv.
6	Dope F	40	200	1.5	-0.8	B	5	25	20	Comp.
7	Dope G	40	255	2.4	-1.5	A	6	20	20	Comp.

Inv.: Inventive, Comp.: Comparative

As is apparent from Table 1 above, inventive cellulose ester film samples provided a low moisture vapor transmittance, excellent rate of weight change, and excellent dimensional stability, although they had a reduced thickness. Further, inventive cellulose ester film samples were confirmed to give film having a low retardation in plane (Ro). In contrast, comparative cellulose ester film sample 6 provided a poor rate of weight change and a poor dimensional stability. Further, comparative sample 6 was confirmed to give a film which was extremely poor in resistance to UV light, resulting in discoloration due to UV irradiation and breakage due to folding after UV irradiation. It was confirmed that comparative cellulose ester film sample 7 could not provide a sufficiently low moisture vapor transmittance, and provided poor dimensional stability as well as poor rate of weight change.

In inventive cellulose ester film samples 1 through 5, neither discoloration after UV irradiation nor breakage due to folding after the UV irradiation was observed. As is apparent from the aforementioned, in comparative cellulose ester film sample 6, both discoloration after UV irradiation and breakage due to folding after the UV irradiation were observed. That is, it was confirmed that deterioration due

to UV irradiation was caused in the comparative cellulose

ester film sample 6.

Polarizing plates (inventive) were prepared employing

the inventive cellulose ester film samples 1 through 5, which

contained a compound represented by formula (1). The

resulting polarizing plates were evaluated for their

durability, and the results exhibited excellent durability.

In contrast, polarizing plates (comparative) prepared

employing the comparative cellulose ester film sample 6 or 7

exhibited poor durability.

A liquid crystal display employing the inventive

polarizing plates could maintain an initial image contrast

over a long term.

Example 2

Polarizing plate samples were prepared employing the

cellulose ester film samples prepared in Example 1 according

to the procedures described later, and the resulting

polarizing plate samples were evaluated according to the

methods also described later.

Polarizing plate sample 1 (inventive) was prepared

employing a cellulose ester film sample 1 as a polarizing

plate protective film according to the following procedures.

1. Preparation of polarizing film

A 120 μm thick polyvinyl alcohol film was uniaxially

stretched (at 110° C by a factor of 5). The resulting film

was immersed for 60 seconds in an aqueous solution comprised

of 0.075 g of iodine, 5 g of potassium iodide, and 100 g of

water, further immersed at 68° C in an aqueous solution

comprised of 6 g of potassium iodide, 7.5 g of boric acid,

and 100 g of water, washed with water, and dried. Thus, a

polarizing film was obtained.

2. Preparation of polarizing plate

The polarizing film obtained above and a polarizing

plate protective film sample were laminated to obtain a

polarizing plate sample according to the following procedures

1 to 5.

Procedure 1: A cellulose ester film sample 1 prepared in

Example 1 was cut to obtain two specimens with a size of 30

cm (in the mechanical direction) x 18 cm (in the transverse

direction). The resulting specimens were immersed in an

aqueous 2 mol/liter sodium hydroxide solution at 60° C for 90

seconds, washed with water, and dried. Thus, two polarizing

plate protective film samples 1 were obtained.

Procedure 2: The polarizing film obtained above was cut into

a size of 30 cm (in the mechanical direction) x 18 cm (in the

transverse direction), and immersed in a polyvinyl alcohol

adhesive (with a solid content of 2% by weight) for 1 to 2 seconds to form an adhesive layer.

Procedure 3: The excessive adhesive of the adhesive layer on the polarizing film prepared in Procedure 2 was softly removed. The one protective film sample 1 was laminated onto one surface of the resulting polarizing film and further, the other protective film sample 1 was laminated onto the other surface of the polarizing film so that it contacted the adhesive layer of the polarizing film.

Procedure 4: Pressure was applied through a hand roller to the laminate with a polarizing film and protective film samples 1 obtained in the Procedure 3 to remove foams or excessive adhesive from the ends of the laminate. The pressure applied by the hand roller was from 20 to 30 N/cm^2, and the roller speed was 2 m/min.

Procedure 5: The sample obtained in the Procedure 4 was dried at 80° C for 2 minutes in a dryer. Thus, a polarizing plate sample 1 (inventive) was obtained.

Polarizing plate samples 2 through 7 were prepared in the same manner as in polarizing plate sample 1, except that cellulose ester film samples 2 through 7 were used, respectively, instead of a cellulose ester sample 1.

Each polarizing plate sample obtained above was

subjected to high temperature and high humidity treatment at

80° C and 90% RH for 50 hours. Thereafter, a transmittance

and a degree of polarization were measured according to the

following methods.

(Measurement of transmittance)

Spectral transmittances τ (λ) of each polarizing plate

sample were measured at an interval of 10 nm in the

wavelength range of from 400 to 700 nm. A transmittance T of

each sample was obtained from the following equation 1.

Equation 1

$$T = \frac{\int_{400}^{700} P(\lambda) \cdot y(\lambda) \cdot \tau(\lambda) \cdot d\lambda}{\int_{400}^{700} P(\lambda) \cdot y(\lambda) \cdot d\lambda}$$

wherein P(λ) represents a spectral distribution function of a

standard light (C light source), and y(λ) represents a color

matching function based on the 2° viewing field X, Y and Z

system.

The spectral transmittances τ (λ) were measured through

a spectro-photometer SIMAZU UV 2200.

(Measurement of degree of polarization)

A transmittance Tp in parallel of a specimen was measured, the specimen being obtained by laminating two of each polarizing plate sample so that orientation of the polarizing element of one polarizing plate was in the same direction as that of the other polarizing plate. Further, a transmittance Tc in cross of a specimen was measured, the specimen being obtained by laminating two of each polarizing plate sample so that orientation of the polarizing element of one polarizing plate was in the direction normal to that of the other polarizing plate.

The degree of polarization P of each sample was calculated from the following Equation 2.

Equation 2

$$P = \sqrt{\frac{Tp - Tc}{Tp + Tc}} \times 100$$

Durability of polarizing plate

Two polarizing plates with a size of 10 x 10 cm^2 per each polarizing plate sample were cut, and subjected to heating and humidifying treatment at 80° C and 90% RH for 50 hours. Subsequently, one plate was laminated on the other to be arranged in a crossed Nicol state so that the adjacent two sides of one plate were in accordance with those of the other. In the resulting polarizing plate laminate, one plate

was longer than the other by a length, and the edge of the

laminate having the length appeared white. The length of the

edge on the central line of the longer plate was measured,

and durability of the polarizing plate sample was evaluated

according to the following evaluation criteria.

The expression "appeared white" means the phenomenon

that the edge of the longer plate in the polarizing plate

laminate, in which two polarizing plates were arranged in a

crossed Nicol state, transmits light and therefore, appears

white. Such phenomenon can be easily judged by visual

observation. Such phenomenon causes visualization problem in

that images at edge portions cannot be observed in such a

polarizing plate.

Ratings A, B and C are not problematic for a polarizing

plate. Rating D is problematic for practical use. Rating E

cannot be put into practical use for a polarizing plate.

A: The length of one edge turning white was less than 5%.

B: The length of one edge turning white was from 5% to less

than 10%.

C: The length of one edge turning white was from 10% to less

than 20%.

D: The length of one edge turning white was from 20% to less

than 50%.

E: The length of one edge turning white was not less than 50%.

The evaluation described above has been made. The inventive polarizing plate samples 1 through 5 provided a transmittance of not more than 45%, and a degree of polarization of not less than 98%. In contrast, the comparative polarizing plate sample 6 provided a transmittance of 5%, and a degree of polarization of 85%. In the durability evaluation, the inventive polarizing plate samples 1 through 3 were rated as A, and the inventive polarizing plate samples 4 and 5 as B, however, the comparative polarizing plate samples 6 and 7 were rated as D.

As is apparent from the above, the inventive polarizing plate samples exhibited excellent durability as compared with the comparative polarizing plate samples.

Example 3

(Preparation of liquid crystal panel and liquid crystal display sample)

The two polarizing plates were peeled from the both sides of the liquid crystal cell of a commercially available display panel (a color liquid crystal display MultiSync LCD1525J TYPE LA-1529HM, produced by NEC Co., Ltd.). Subsequently, the two of each of inventive polarizing plate

samples 1 to 5 and comparative polarizing plate samples 6 and 7 prepared in Example 2 were superposed on the liquid crystal cell so that their polarizing direction was in accordance with the original one to obtain a liquid crystal panel. The resulting liquid crystal panel was installed in the color liquid crystal display, and contrast was visually evaluated. As a result, it has been confirmed that the liquid crystal panel employing the inventive samples maintained a high contrast for a long term as compared with the liquid crystal panel employing the comparative samples.

EFFECTS OF THE INVENTION

The present invention can provide a cellulose ester film which has a good moisture vapor transmittance, and excellent dimensional stability, even when it has a reduced thickness. Further, the present invention can provide a method of manufacturing the cellulose ester film, and a polarizing plate and a liquid crystal display each employing the cellulose ester film.